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Electronic-shell effects in small doubly charged lead clusters

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Lead-cluster mass spectra, the lead clusters being generated by the gas aggregation technique and ionized by electron impact, reveal, besides the well-known relative abundance maxima for singly charged species, relative concentration maxima for the doubly charged ones. Among the most intense peaks the following ones for $\mathrm{Pb}_n{}^{2+}$: $n=9$, 15, 23, 27, and 35 were found. Since lead is tetravalent, the total numbers of valence electrons for the above-mentioned ions are 34, 58, 90, 106, and 138 per cluster (i.e., $4n-2$), respectively. These numbers are exactly those for which the shell closing of the valence electrons within a spherically symmetric potential is achieved. This result demonstrates the importance of electronic effects on the stability, not only for neutral and singly charged metal clusters, but also for doubly charged ones.

INTRODUCTION

Recent experimental results concerning the stability of neutral as well as singly positively and negatively charged metal clusters demonstrate the importance of electronic effects.[1,2] Besides the well-known odd-even effect (stabilization by electron-spin pairing) the shell-like arrangement of valence electrons has also been widely discussed.[1,3,4] At shell closing the cluster reaches a higher stability compared to the adjacent ones, giving rise to concentration maxima in the cluster spectra. On the other hand, especially for van der Waals clusters, it is known that geometrical effects govern the stability. Like an inert gas crystal, lead has a close-packed crystal structure. Dense sphere packing as well as electronic effects are responsible for the occurrence of concentration maxima and minima in the lead cluster-mass spectra of the singly charged species.[5,6,7] The importance of electronic effects in small lead clusters has also been demonstrated by photon-emission spectroscopy experiments.[8]

Recently, doubly charged lead clusters $\mathrm{Pb}_n{}^{2+}$ ($n \geq 3$) generated by a gas aggregation technique could be observed continuously during the experimental time scale of a few μs.[9] The stability and/or metastability of doubly charged metal clusters is still a question being intensively investigated both theoretically and experimentally. *Ab initio* calculations of Koutecký *et al.*[10] showed, for example, that $\mathrm{Li}_6{}^{2+}$ and $\mathrm{Li}_8{}^{2+}$ are metastable, the fragmentation into two charged species being hindered by the existence of a potential barrier. A similar result for $\mathrm{Be}_n{}^{2+}, n \leq 5$, was obtained by Khanna *et al.*[11] using a local-spin-density formalism. Recently, even the existence of $\mathrm{Au}_2{}^{2+}$ generated by a liquid-metal ion source has been demonstrated, indicating that in the case of noble-metal clusters the *d* electrons must also be considered.[12]

As has been demonstrated by Hoareau *et al.*[13] for Pb and by the authors for Pb, Ag, Bi, and Au[9] it is necessary to shift the mean size of the neutral distribution into a suitable mass range with sufficient intensities thus to be able to observe small doubly charged species. In this paper we report on distinct stability maxima among charged $\mathrm{Pb}_n{}^{2+}$ clusters.

EXPERIMENT

The clusters were generated by means of the gas aggregation technique, which allowed us to create narrow cluster-size distributions with mean sizes ranging from a few atoms to about 10^4-10^5 atoms per cluster. Using this technique it was possible to shift the mean size of the distribution into a suitable mass range allowing us to maximize the intensity of the small doubly charged species. A detailed description of the cluster-source parameters is given elsewhere.[9,14] In short, metal is vaporized from a Knudsen cell into an argon atmosphere where cluster growth occurs under conditions of high supersaturation via homogeneous nucleation. A cluster beam is formed by apertures within a helium-cooled differential pumping unit. For analysis, this beam is directed along the ion optical axis of a single focusing mass spectrometer. The spectrometer is a modification of the type SM1A (Varian-MAT).[15] The electron impact ionization source is a modified Nier-type source.[16] The spectra presented here are obtained with a counting device (multichannel analyzer).

RESULTS AND DISCUSSION

Figure 1 presents three lead-cluster mass spectra of different neutral-size distributions. For all cases the ionization conditions are the same: $E_i = 100$ eV, $I = 100$ μA. The mean size of neutral clusters as well as the counting rate increases from top to bottom. This was achieved by increasing the metal evaporation rate, as discussed in detail recently.[9] For a small mean size of the neutral-size distribution [Fig. 1(a)] the intensities of the singly charged species are low and only some larger doubly charged clusters are present. Shifting the mean cluster size to higher values [Fig. 1(b); approximately 30 atoms per cluster] results in the appearance of a doubly charged species $\mathrm{Pb}_n{}^{2+}$, $n \geq 3$, and trace amount of a triply charged species Pb_n^{3+}, $n \geq 49$. It should be noticed that only in this spectrum are concentration maxima along the doubly charged lead clusters observed. A further shift to a larger mean cluster size [Fig. 1(c)] results in a further increase of the total intensity, the smaller singly charged clusters, however, lose intensity compared to the larger ones. Additionally, triply charged clusters Pb_n^{3+} appear clearly for $n \geq 43$ and the relative intensity of the doubly charged species decreases compared to that so singly charged ones, now showing a more or less continuous structureless intensity growth towards larger masses.

The appearance of concentration maxima of singly, as well as doubly, charged species will now be discussed in more detail. The concentration maxima of the singly charged clusters (Fig. 1) at Pb_n^+, $n=7$, 10, 13, 17 and 19, are well known from literature.[6,7,13,17] (19 is not clearly seen here to be magic due to our limited mass range.) It should be remembered that pentagonal bipyramide ($n=7$) isocahedron ($n=13$), and capped isocahedron ($n=19$) structures have been invoked to explain the stability of the neutral clusters, while "electronic" effects are used to explain the relative stability of the neutral clusters ($n=10,17$).[5] The lead atom has the electronic configuration $6s^2 6p^2$. Since, on the one hand, these states form the valence band in bulk Pb, and on the other hand, the atomic Pb is mostly tetravalent in chemical reactions, we assume that both p and s electrons of lead build the valence shell in clusters.[18] In that case Pb_{10}^0 and Pb_{17}^0 clusters have 40 and 68 valence electrons, respectively. These values are shell-closing numbers for neutral "nearly free-electron gas" clusters within the spherical shell model[1,3,4] filling the $2p$ and $2d$ shell, respectively (see Table I), i.e., the higher intensities of these ionic clusters reflect higher abundances of the corresponding neutral clusters in the incident beam. Distinct maxima for doubly charged species Pb_n^{2+} in Fig. 1(b) are found for $n=15$, 27, and 35; additionally, more or less clear steps occur for $n=9$ and 23. Neutral species Pb_n^0 ($n=9,15,23,27,35$) possess $4n$ valence electrons, i.e. 36, 60, 92, 108, and 140 electrons while Pb_n^{2+} have $4n-2$ electrons, i.e., 34, 58, 90, 106, and 138. Table I shows the ordering of the electron shells for different quantum numbers n,l—calculated within a jellium model using a spherical square-well potential[19]—together with the total number of electrons necessary to achieve shell closing. The ordering of shells corresponding to the same scheme was found in neutral and singly charged alkali-metal clusters[20,21] and single (positively and negatively) charged noble-metal clusters.[2,21,22]. In addition the theoretical investigation based on the self-consistent spherical jellium model shows that the ordering of shells for neutral, singly, doubly, and triply charged clusters is the same.[23]

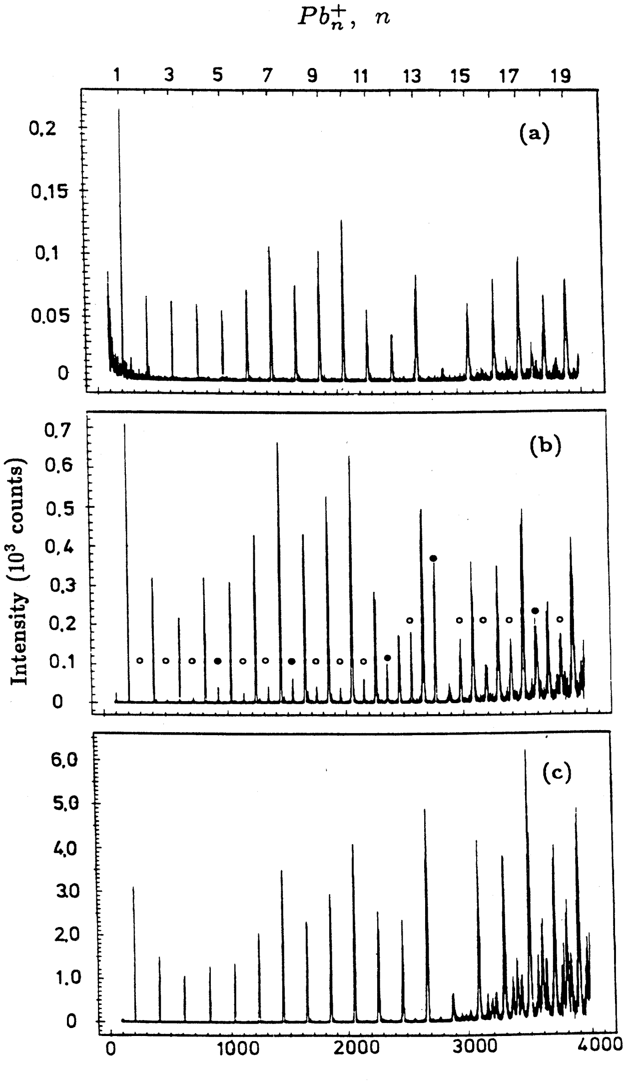

FIG. 1. Mass spectra of lead clusters for different neutral-size distributions at electron impact energy $E_i=100$ eV (increasing size from top to bottom). In (b) all doubly charged clusters are indicated by circles; the magic ones by solid circles.

From the comparison of the data given in Table I with our experimental results it is obvious that excellent agreement exists for the values found within the $4n-2$ series. For these "magic" numbers the $1f$, $1g$, $1h$, $2f$, and $3p$ shells are filled. Thus two conclusions can be drawn simultaneously. (a) The particularly stable doubly charged clusters do not originate from the particularly stable neutrals, but are a consequence of the electronic structure of doubly charged species; (b) the ordering of shells in the doubly charged species is the same as the one previously found in the neutral and singly charged ones.

Due to the low resolution of our mass spectrometer[15] it is not possible at the present time to separate the contribution of doubly charged even clusters from the intensity at the positions of the singly charged ones by making use of the given isotopic composition of lead. Although an exact shell closing for other shells given in Table I (name-

TABLE I. Ordering of electron shells for different quantum numbers n,l along with total number of electrons necessary for shell closing.

1s	1p	1d	2s	1f	2p	1g	2d	1h	3s	2f	1i	3p
2	8	18	20	34	40	58	68	90	92	106	132	138

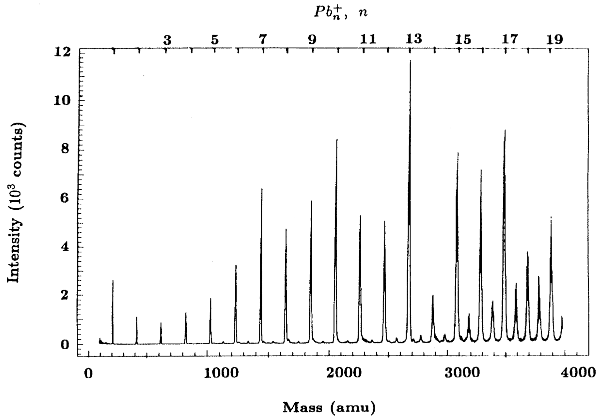

FIG. 2. Mass spectrum of lead clusters of the same size of neutral clusters underlying 1(c) at electron impact energy $E_i = 50$ eV.

ly, $2p$, $2d$, $3s$, and $1i$ where the corresponding number of electrons is divisible by 4) cannot be reached within the $4n-2$ series, it would be helpful to follow the filling of different shells for each cluster Pb_n^{2+} since for not "totally magic" clusters relative differences of intensities can also be expected. It is interesting to note that te observed magic numbers for doubly charged lead clusters Pb_n^{2+} for $n=9$, 15, 23, 27, and 35 are already theoretically expected and calculated explicitly for Pb_n^{2+}.[24] Analogous results are theoretically obtained for Na_n^{2+} and Mg_n^{2+}.[25]

In the following the most probable fragmentation mechanism of the neutral as well as of doubly charged clusters leading to the spectrum presented in the Fig. 1(b) will be discussed briefly. Since the corresponding neutral clusters are not expected to be of higher intensities compared to the adjacent ones in the neutral cluster beam—they don't possess magic numbers of electrons ($4n$, compare Table I)—it must be assumed that magic ionic species represent favored fragmentation products. In order to get some insight into the fragmentation process following electron impact ionization, experimental conditions were chosen under which triply charged clusters as seen in Fig. 1(c) are also present. The change of spectra pattern as a function of electron impact energy was investigated. Figure 2 shows a spectrum obtained under conditions identical with those for the spectrum given in Fig. 1(c), except that the electron impact energy was decreased from 100 to 50 eV. A drastic decrease of the smaller singly charged species compared to the larger ones can easily be recognized. This behavior reflects the experimentally and theoretically well-established fragmentation behavior of singly charged metal clusters by evaporation of neutral monomers and dimers.[26,27] The intensity pattern of the doubly charged clusters in Fig. 2 remains essentially unchanged whereas the triply charged clusters are not present. This finding may be taken as evidence that the observed doubly charged clusters in Fig. 1(b) are not fragmented from triply or higher charged species. We therefore suggest direct ionization followed mainly by neutral monomer-dimer evaporation to be responsible for the observed doubly charged clusters Pb_n^{2+} of Fig. 1(b) in analogy to the fragmentation of singly charged species within the given time scale of these experiments.

In conclusion, we have shown experimentally that the effective number of valence electrons plays a dominant role in the stabilization of doubly charged clusters. The most stable cluster ions are found to possess magic numbers of valence electrons as predicted by calculations, indicating the applicability of the jellium-shell model to an element of group 4 where more localized bonding occurs. This result may be interpreted as evidence of metallic nature of even small lead clusters.

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